Separation of gas mixtures using Co(II) carborane-based porous coordination polymers†

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Separations of CO_2/CH_4, CO_2/N_2, and O_2/N_2 mixtures were studied in three porous coordination polymers made of the same carborane ligand and Co(II) nodes. High selectivities for CO_2 over CH_4 (~47) and CO_2 over N_2 (~95) were obtained, especially in the material with coordinated pyridine. Unusual selectivity for O_2 over N_2 (as high as 6.5) was demonstrated in the materials with open Co(II) sites.

Separation of gas mixtures by adsorption is very important in industry. Currently, porous materials such as zeolites and activated carbons are generally used as adsorbents for selective adsorption.[1] Porous coordination polymers (PCPs), also referred to as metal–organic frameworks (MOFs), are an emerging new class of materials that have shown significant promise for gas and small molecule storage.[2] However, significantly less work has been done to investigate the separation properties of this class of materials.[3] An attractive feature of porous coordination polymers lies in the rational and highly versatile synthetic strategies that form these materials. A typical synthesis relies on the use of simple metal salt precursors and organic ligands as building blocks. Usually a solvothermal process is used to facilitate the formation of extended porous networks from simple metal ion precursors and interconnecting ligands. We have been interested in constructing such coordination polymers from icosahedral carboranes due to their inherent robustness, which results in porous materials with thermal stability and resistance towards collapse under harsh conditions.[4] To this end, we recently introduced an example of Co(II) carborane-based porous coordination polymers with tunable morphology and structure. Different coordination polymer structures were obtained depending on the solvent, and the materials show drastically different N_2 and H_2 uptake as a result of their varied porosities.[5] This prompted us to explore the capabilities of these materials for gas separations.

Herein, we report a study of the gas separation properties of Co(II) carborane coordination polymers. This study demonstrates how the adsorption selectivities of a set of materials made of the same ligand and metal can be dram atically different, depending on the structural nature of the porous polymer.

Carborane-based ligand **2** (1,12-dihydroxy-carbonyl-1,12-dicarba-*closo*-dodecaborane) can be synthesized in one step on a multi-gram scale from commercially available p-carborane **1**. Two coordination polymer materials were made *via* solvothermal reaction of compound **2** and cobalt(II) salts (Fig. 1A). Depending on whether a dimethylformamide (DMF)/ethanol mixture or a pyridine/water/1-butanol mixture was used, two structurally distinct materials (**3**: $[Co_4(OH)_2(\mathbf{2})_3DMF_2]$; **4**: $[Co(\mathbf{2})(pyridine)_2(H_2O)]$) were synthesized, as primarily evidenced from X-ray diffraction studies (Fig. 1B and C).[5] Changes in the coordination environment affected the metal cluster core (commonly referred to in MOF chemistry as a secondary building unit, SBU) mode, leading to different 3-D arrangements at the SBU.[5] Interestingly, the complexes with these coordination modes are quite different from each other with respect to their magnetic behavior. For example, SQUID magnetization measurements revealed a distinct anti-ferromagnetic ordering in **4**, whereas no such behavior was observed in **3** (Fig. 2A).

Solvents play an essential role in the synthesis of this class of materials, since certain solvent molecules (*e.g.* DMF and pyridine) can compete with building block ligands for metal sites and lead to different structures. Thermogravimetric analysis (TGA) indicates that both **3** and **4** are stable up to approximately 400 °C. For both materials, solvent loss, due to trapped molecules in the voids of the network, is observed (100–130 °C), which is followed at higher temperatures (200–250 °C) by a loss of the coordinated DMF and pyridine species in **3** and **4**, respectively.[5] Thus, by activating **3** and **4** at 300 °C, we could obtain solvent-free **3a** and **4a**. These materials presumably have open Co(II) sites in the pores, based on similar behavior in other coordination polymers.[4b] If **4** is activated at 120 °C, **4b** containing pyridines coordinated by Co(II) can be created (Fig. S2†).

We have previously established that **3a** and **4a** have different pore volumes (0.42 and 0.14 $cm^3\ g^{-1}$, respectively).[5] For **4b**, almost no N_2 adsorption is observed at 77 K, which implies that **4b** with coordinated pyridines has slightly more constricted pores than **4a**. Given that these materials have such dramatic differences in their porosity, we decided to investigate gas separation properties for **3a**, **4a**, and **4b**. Since these compounds

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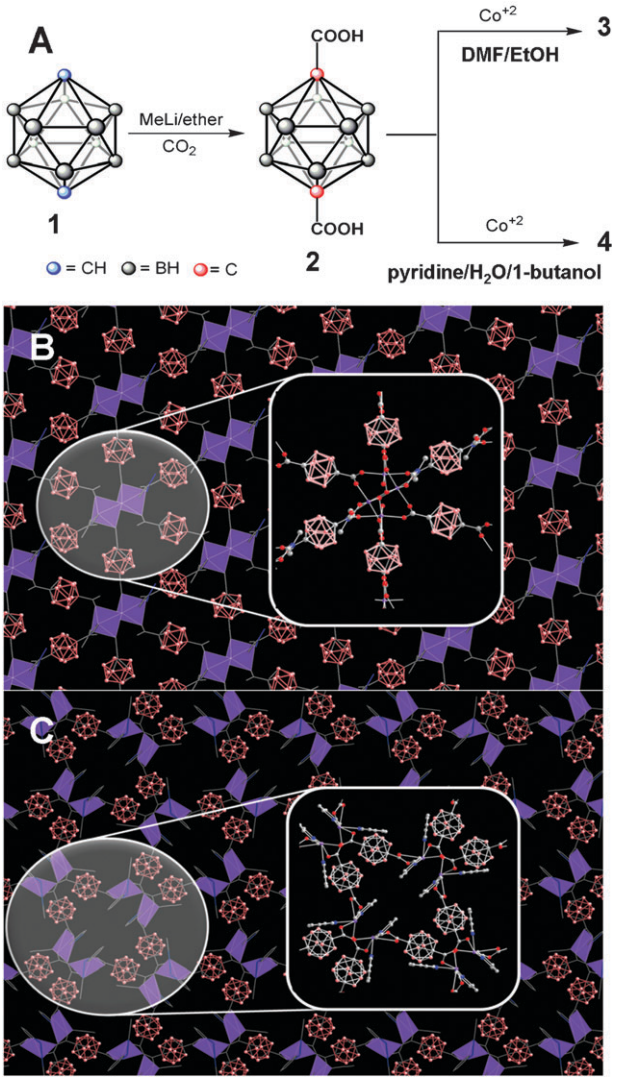

Fig. 1 (A) Syntheses of carborane ligand precursor and its corresponding polymers **3** and **4**. (B)–(C) Crystallographically derived representations of the 3-D networks of **3** and **4**, respectively. H atoms and solvents have been omitted for clarity. C, gray; O, red; N, blue; Co, purple; B, salmon.

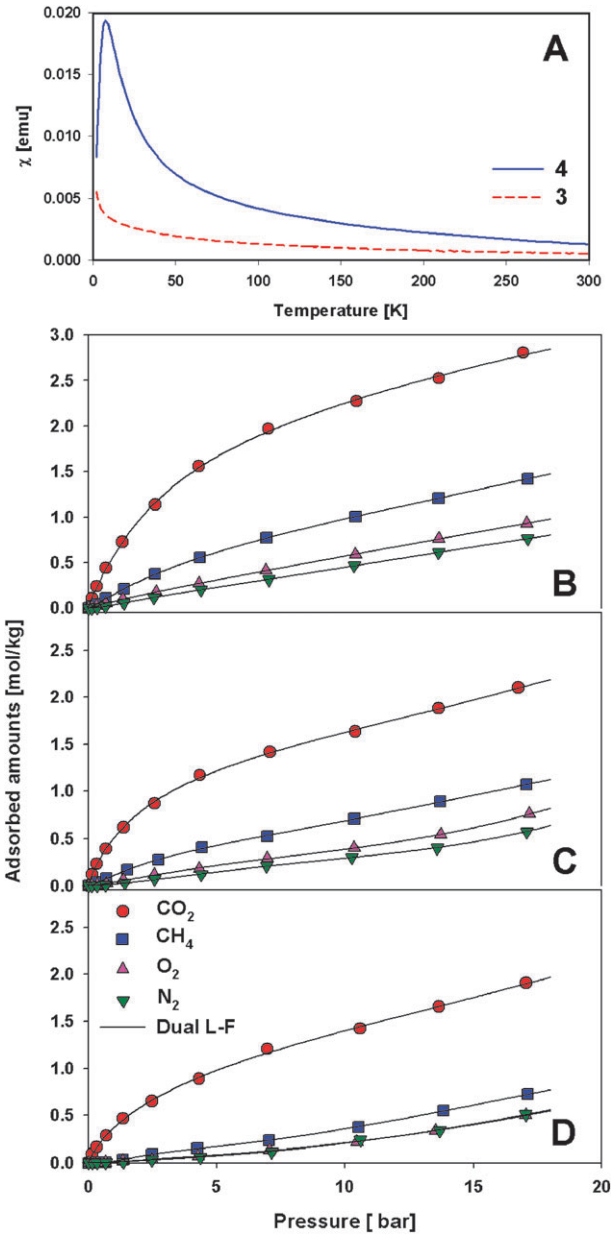

Fig. 2 (A) Temperature dependent field-cooled magnetization measurements of **3** and **4**. (B)–(D) Single-component isotherms of CO_2, CH_4, O_2, and N_2 in **3a**, **4a**, and **4b**, respectively. Solid lines indicate fits from the dual-site Langmuir–Freundlich (Dual L–F) equation.[6]

have polar Co(II) sites, we hypothesized that these materials might facilitate selective adsorption of quadrupolar CO_2 over nonpolar CH_4 or weakly quadrupolar N_2. The separation of CO_2 from methane is essential in natural gas upgrading,[6,7] and the separation of CO_2 from nitrogen is needed for flue gas emissions of power plants to capture the greenhouse gas CO_2.[8] Also, it has been reported that Co(II) may be useful for selective O_2 adsorption from air,[9] which is also addressed in our study. O_2 of various purities is needed in industry for applications such as semiconductors, combustion systems, and medicine.[10]

Pure isotherms of CO_2, N_2, CH_4 and O_2 for **3a**, **4a** and **4b** at 298 K and pressures up to 17 atm were measured, based on previously established methods.[6] In Fig. 2B and C, **3a** and **4a** show similar adsorption trends ($CO_2 > CH_4 > O_2 > N_2$), and this may be explained by the similar framework components (the carborane ligand and the open Co(II) sites) in both materials. But, **3a** shows slightly greater adsorption due to the larger pore volume. A remarkable point is that **3a** and **4a** show rarely observed selective adsorption of O_2 over N_2. This does not originate from molecular sieving, because the larger molecule CH_4 adsorbs readily in the pores of **3a** and **4a**. We suggest that this may come from the strong interaction between O_2 and coordinatively unsaturated Co(II) in the pores of **3a** and **4a**. On the contrary, **4b** shows very similar O_2 and N_2 adsorption because it does not have coordinatively unsaturated Co(II) (Fig. 2D). In addition, **4b** shows very little N_2, O_2, and CH_4 adsorption at low pressures compared to CO_2. The constricted pores of this sample may be the reason for this observation; CO_2 molecules (3.3 Å) can adsorb at low pressures but the larger molecules (O_2: 3.46 Å; N_2: 3.64 Å; CH_4: 3.82 Å) cannot.[11]

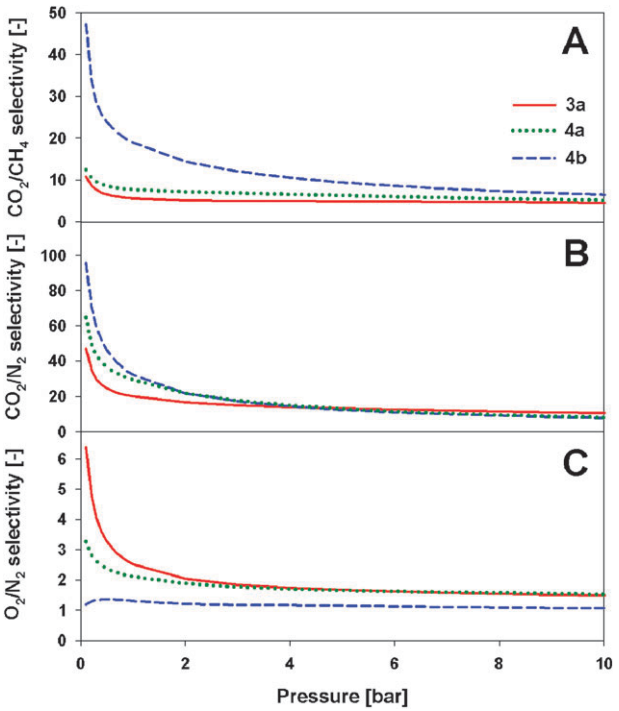

Fig. 3 Selectivities for three materials at equimolar mixture conditions. (a) CO_2 over CH_4, (b) CO_2 over N_2, and (c) O_2 over N_2.

The adsorption selectivities for mixtures of CO_2/CH_4, CO_2/N_2 and O_2/N_2 were predicted from the experimental pure isotherms using the ideal adsorbed solution theory (IAST). Previous studies have shown that the IAST can predict the behavior of simple gas mixtures in MOFs from single-component isotherms.[6,12,13] The predicted selectivities for equimolar gas mixture pairs in **3a**, **4a**, and **4b** are compared in Fig. 3. A remarkable point is that **4b** shows very high CO_2/N_2 ($\sim$95) and CO_2/CH_4 ($\sim$47) selectivities. This can be explained by the size selective pores of **4b** as mentioned above. Under similar conditions, these selectivities are considerably higher than those of other adsorbent materials: (1) CO_2/N_2 – a cobalt adeninate MOF (75),[8d] ZIF-78 (50),[14] a cavity modified MOF (41),[8a] zeolite 4A (19),[15] activated carbon (15);[16] (2) CO_2/CH_4 – a mixed-ligand MOF (30),[6] a carborane-based MOF with open metal sites (17),[7] a 2-D MOF with open metal sites (13),[17] ZIF-78 (10),[14] zeolite β (28).[18]

Compared to **4b**, materials **3a** and **4a** show smaller CO_2/N_2 and CO_2/CH_4 selectivities due to their larger pores. Nevertheless, the CO_2/N_2 selectivities of both materials are still large (**3a**: $\sim$47; **4a**: $\sim$65). Moreover, **3a** and **4a** show remarkable O_2/N_2 selectivities (**3a**: $\sim$6.5, **4a**: $\sim$3.5), which are not observed in **4b**. As mentioned earlier, this can be explained by the presence of coordinatively unsaturated Co(II) in **3a** and **4a**, which is absent in **4b**. Such oxygen selective behavior is unusual for zeolite and MOF-type materials. Several recent papers report selective adsorption of O_2 over N_2 in coordination polymers due to molecular sieving,[19a–d] but we are aware of only one other example in the absence of molecular sieving.[19e] Li and Yang report a very mild O_2/N_2 selectivity of 1.8 in MOF-177,[19e] but its origin is not well understood. The coordinatively unsaturated Co(II) sites in **3a** and **4a** provide a possible explanation for the improvement to 6.5.

In summary, our experiments and IAST calculations have shown that **4b** shows very large CO_2/CH_4 and CO_2/N_2 selectivities while **3a** and **4a** show unusual O_2/N_2 selectivities due to the presence of coordinatively unsaturated Co(II) sites. This shows that the adsorption selectivities can be changed dramatically in coordination polymers made of the same ligand and metal, depending upon the activation conditions and resulting pore structure.

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